

(12) **UK Patent Application** (19) **GB** (11)

2 139 224 A

(43) Application published 7 Nov 1984

(21) Application No **8410823**

(22) Date of filing **27 Apr 1984**

(30) Priority data

(31) **8307305**

(32) **29 Apr 1983**

(33) **FR**

(51) INT CL³

C07C 29/15 31/04

(52) Domestic classification

**C2C 20Y 229 30Y 360 361 36Y 408 411 413 414 415 416 50Y
566 567 568 623 65Y JM YK**

(56) Documents cited

None

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(58) Field of search

C2C

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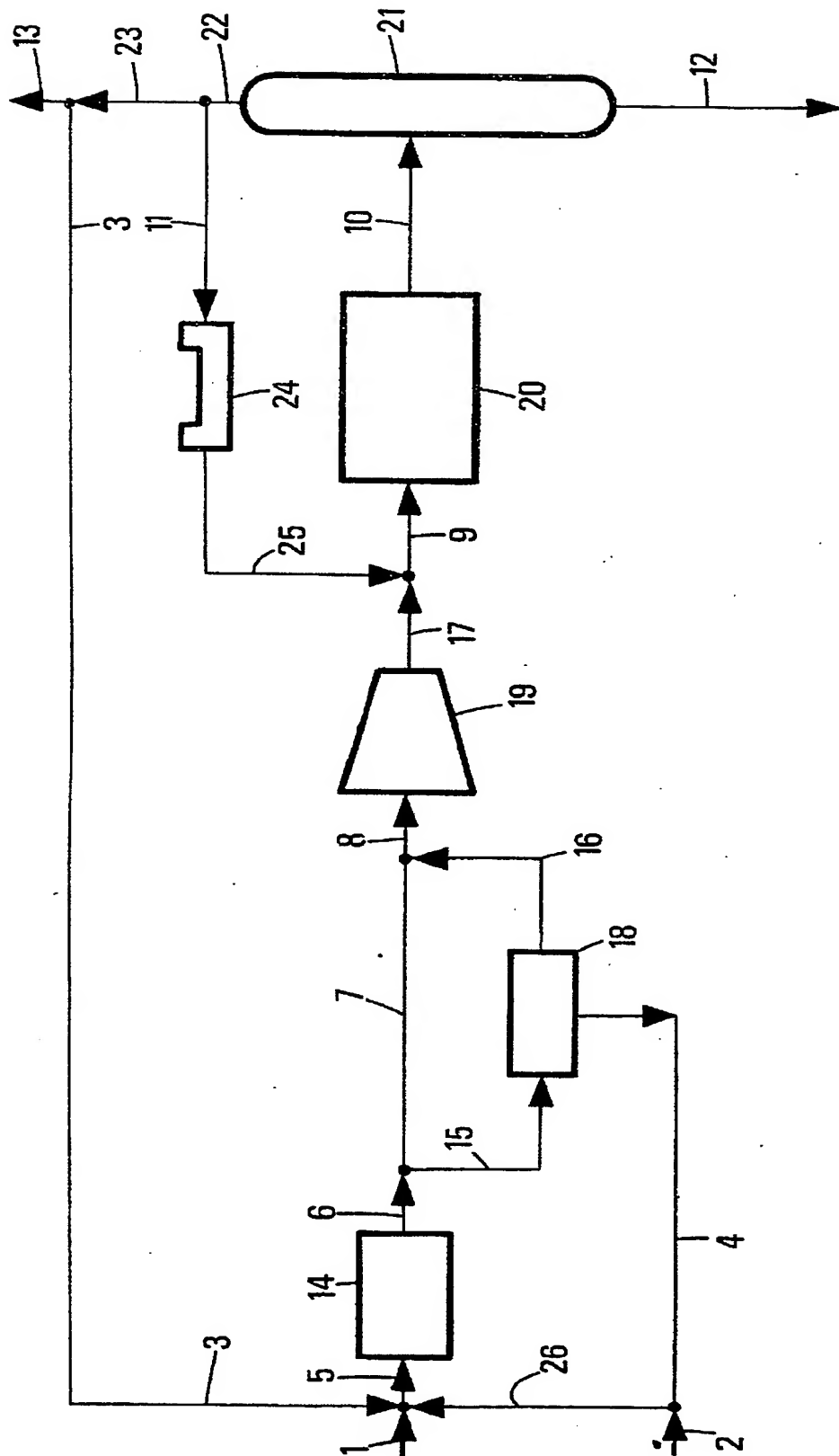
(54) **Producing alcohols from lower hydrocarbons**

(57) A mixture of methanol with higher alcohols is obtained by coupling a hydrocarbon steam-reforming reaction with an alcohol synthesis reaction using a synthesis gas produced in the steam-reforming zone, at least a portion of the carbon dioxide and the light hydrocarbons present in the gas phase withdrawn from the alcohol synthesis zone being recycled to the steam-reforming zone.

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SPECIFICATION

Process for producing alcohols from light hydrocarbons

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This invention relates to a process for producing a mixture of methanol with at least one higher alcohol.

Methanol and its higher homologues such as linear and saturated alcohols containing for example 2 to 10 carbon atoms per molecule (e.g. ethanol, propanol, butanols, and pentanols), as well as mixtures thereof, can be used as gasoline components which can be directly added to a gasoline base essentially consisting of hydrocarbons (i.e. a motor gasoline of normal type or of premium grade) so as to obtain, for example, a motor gasoline of excellent quality at a moderate price.

Methods for producing alcohol mixtures from synthesis gases, in one or more steps, have been extensively described in the prior art, for example in French Patent Application No. 82/16 345 of September 23, 1982, British Patent No. 2 120 119, French Patent No. 2 523 957, French Patent Application No. 82/11 892 of July 5, 1982 and French Patents Nos. 2 369 234 (or USP No. 4 122 110), No. 2 444 654 (or USP No. 4 291 126), No. 2 453 125 and No. 2 441 420.

According to the present invention there is provided a process for producing a mixture of methanol with at least one higher alcohol said process comprising the steps of:

a) passing a mixture of a least one fresh hydrocarbon having 1-4 carbon atoms with steam, a carbon dioxide stream and a first recycle gas stream through a steam-reforming zone at 650-950°C, so as to obtain a synthesis gas comprising hydrogen, carbon monoxide and carbon dioxide,

b) separating a carbon dioxide stream from said synthesis gas and passing a mixture of resultant synthesis gas of decreased carbon dioxide content with a second recycle gas stream through an alcohol synthesis zone,

c) separating the product from step (b) into a liquid phase comprising water and at least the major portion of the alcohols formed in step (b) and a gas phase comprising hydrogen, carbon monoxide, carbon dioxide and hydrocarbons,

d) dividing the gas phase from step (c) into at least a first gas stream and at least a second gas stream, said first gas stream amounting to 2-15% by volume of said gas phase from step (c) and said second gas stream amounting to 85-98% by volume of said gas phase from step (c),

e) feeding said first gas stream of step (d) to step (a), as said first recycle gas stream and controlling the ratio of said first recycle gas stream to said fresh hydrocarbon passed through said steam-reforming zone to have a molar ratio of hydrocarbon in said first recycle gas stream to said fresh hydrocarbon between 0.2 and 2 and to obtain a molar ratio of hydrogen to carbon monoxide in the synthesis gas obtained in step (a) from about 2 to 3,

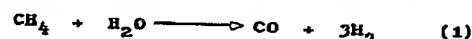
f) feeding said second gas stream of step (d) to

step (b) as said second recycle gas stream and controlling the proportion of said second recycle gas stream to have a molar ratio of hydrogen to carbon monoxide in said mixture passed through said alcohol synthesis zone from 1.6 to 2.4, and

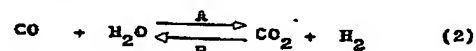
g) admixing said carbon dioxide stream of step (b) with said fresh hydrocarbon of step (a) to constitute at least a portion of said carbon dioxide stream of step (a).

The process according to the invention essentially comprises two stages; the first stage is a steam-reforming, i.e. a reaction of water with methane or light hydrocarbon gases (LPG) of formula C_nH_{2n+2} with $n = 1$ to 4. This reaction generates a synthesis gas comprising carbon monoxide, carbon dioxide and hydrogen which can be used, in the second stage, to produce one or more alcohols.

Such a process does not seem, *a priori*, economically reasonable for thermodynamic reasons. Thus, the reaction (1) of methane reforming with water:



takes place with the equilibrium (2)



In general, the equilibrium is essentially displaced in the direction A as a result of using an excess of water in reaction (1), which excess is required to avoid coking (by excessive heating) of the reactor and of the catalyst. This leads to a molar ratio of H_2/CO in the product very often ranging from 4.5 to 6. The displacement of the equilibrium (2) in the direction A thus results in a hydrogen content which is too high and which in the second stage results in a too large production of methane, to the prejudice of the desired alcohols.

This displacement in the direction A is the more unfavorable as, at the temperatures generally used, even in the absence of a water excess, the value K_p (direction A) of the equilibrium is in favor of the displacement in the direction A, which results in an excessive and detrimental production of CO_2 .

The various values of K_p at different temperatures are indicated below:

$$K_p \text{ (direction A)} = \frac{p_{CO_2} \cdot p_{H_2}}{p_{CO} \cdot p_{H_2O}}$$

T°K	T°C	Log ₁₀ K _p	K _p
298	25	4.992	98175
300	27	4.947	88512
400	127	3.166	1466
500	227	2.114	130.0
600	327	1.429	26.85
700	427	0.952	8.95
800	527	0.603	4.01
900	627	0.341	2.19
1000	727	0.136	1.37

The invention is based on the injection of CO₂ into the first reactor. This injected CO₂ may be supplied at least partly from stored compressed CO₂, from an adjacent process unit (e.g. for ammonia synthesis), from an oil or natural gas field, by recovery from the fumes of a steam-reforming furnace, or the like, but, according to the invention, at least a portion of the CO₂ is advantageously withdrawn from the subsequent alcohol synthesis reactor. This use of the CO₂ obtained from the alcohol synthesis reactor overcomes numerous difficulties resulting generally from the presence of CO₂ in the gases withdrawn from the synthesis reactor. Thus, it is desirable to recycle these gases to the synthesis reactor, but the presence of CO₂ in said gases has disadvantages for the reasons discussed below.

In order to synthesize alcohols from carbon monoxide and hydrogen, a theoretical amount of two moles of hydrogen is required per mole of CO, according to the reaction (3):



Thus, for this type of reaction, it is generally desirable to proceed with a molar ratio of H₂/CO of about 2, for example from 1.6 to 2.4 and more particularly from 1.8 to 2.2, which will be made possible by the process of the invention.

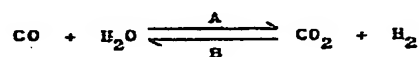
In the prior art processes, generally the synthesis gas is obtained by gasification of coal, coke, heavy oil residues, bitumen, etc... and its composition does not correspond to the stoichiometrical composition for obtaining alcohols, this synthesis gas having a too low hydrogen content; its composition must hence be adjusted by steam-conversion of CO followed with the removal of at least a part of the formed CO₂. As a matter of fact, it is preferable to limit the CO₂ amount in the synthesis gas, since the synthesis of alcohols from CO₂ requires more hydrogen than the synthesis from CO (reaction (4)):



During the synthesis of alcohols, the recovered reaction effluent contains unconverted gases (CO + H₂), methanol, water, hydrocarbons (methane and heavier hydrocarbons having at least 2 carbon atoms per molecule) and methanol homologs. This whole effluent is cooled, so as to condense a major part of methanol and homologous alcohols and the major part of water. The uncondensed fraction essentially contains carbon monoxide, hydrogen, methane, other hydrocarbons and carbon dioxide. This gaseous fraction, in the prior art, is recycled at least partly to the reactor input as additional gas for increasing the molar ratio H₂/CO (at the input of the synthesis reactor) to a value of at least 1.8 and preferably about 2.

But the process, as just described, has the major disadvantage resulting from the presence of relatively substantial carbon dioxide amounts in the gas withdrawn from the reactor. As above explained, the production of alcohols from CO₂ requires more hydrogen than from CO. A recycling of CO₂ is hence finally undesirable. Moreover the CO₂ recycling to the reaction zone is detrimental to the equilibrated

reaction (2) which also exists for this alcohol synthesis,



said reaction taking place in the reaction zone.

Accordingly, in the prior art, it was often necessary to adopt a time-consuming decarbonation of the uncondensable gases, obviously resulting in a non negligible loss of carbon.

In some of the prior art processes, such a decarbonation was avoided, essentially in methanol manufacture: thus, according to US Patent No. 3 763 205, gases (including CO₂), present in the effluent from the methanol synthesis zone, are recycled to the steam-reforming reactor and exclusively to this reactor and the French Patent No. 2 027 392 provides for two possible recyclings of carbon dioxide-containing gas to the steam-reforming reactor and to the alcohol synthesis reactor. However, in these two patents, the so-recycled gases contain large amounts of hydrogen so that, on the one hand, the ratio H₂/CO at the output of the steam-reforming zone is too high to comply with the stoichiometry of the alcohol synthesis reaction in the second zone and, on the other hand, the too high hydrogen amounts involved further result in an excessive formation of methane in the alcohol synthesis reactor, to the prejudice of the desired alcohols.

The process according to the invention improves the gas recycling techniques for manufacturing methanol and the higher homologous alcohols. In this way, the process avoids decarbonation of the uncondensed gases at the output of the alcohol synthesis zone. Carbon dioxide is used deliberately with the other gases (CO, H₂) and the residual methane accompanying it, to displace the equilibrium (2) in the direction of B, so that in the process of the invention it is possible to convert a major part (e.g. at least 90%) or even 100% of the fresh carbon involved in the process (CO₂ and CH₄) to alcohols. It has been found that generally the gases withdrawn from the steam-reforming zone do not require any cooling before their input into the synthesis reactor.

In the process of the invention the gases from the alcohol synthesis reactor effluent are generally at a temperature of about 100 to 200°C or more and they may be heated to a temperature of about 650 to 950°C (preferably 730 to 890°C) before at least partially recycling them to the steam-reforming reactor operating between 650 and 950°C, preferably between 730 and 890°C, thus acting on the value of K_p to advantageously displace the equilibrium (2) in the direction B.

The process of the invention essentially consists of steam-reforming at a high temperature at which a CO₂ addition is beneficial and an alcohol synthesis reaction supplying CO₂, which is detrimental to said reaction, and light hydrocarbons, but which are advantageously recycled both to the steam-reforming reactor and to the synthesis reactor. The recycled gases are substantially free of water and alcohols. The essential advantages of the present process are thus the following:

— It is no longer necessary to decarbonate the

uncondensable gases issued from the alcohol synthesis reactor,

– The equilibrium (2) of the steam-reforming reaction is displaced in the direction B since the recycled CO_2 , injected in the steam-reforming zone, reacts with the hydrogen produced in the steam-reforming reaction. This displacement in the direction B will decrease the molar ratio H_2/CO (usually too high, of a value from 4.5 to 6) to a value of about 2 to 3 (preferably 2.2 to 2.8) so that, during said reaction of the first step (steam-reforming) little CO_2 but essentially a mixture of CO and hydrogen in a molar ratio from 2 to 3 (preferably 2.2 to 2.8) will be produced, said mixture being ideally adapted for use in alcohol synthesis during the second step. It should be observed that the above-mentioned values of the ratios H_2/CO , as necessary for a good operation of a reactor for synthesizing methanol homologs, substantially differ from the high values of such H_2/CO ratios as disclosed in the US Patent No. 3 763 205 and the French Patent No. 2 027 392.

– In the total balance of these two reactions (steam-reforming and alcohol synthesis) no carbon loss occurs since the CO_2 present is no longer removed but fed to the first step. By coupling the two reactions, all the carbon involved is converted to alcohols. Finally, the light hydrocarbons, by-products of the reaction, which may be formed simultaneously with the alcohols in the synthesis reactor, are accordingly advantageously recycled, together with CO_2 , to the steam-reforming reactor. These light hydrocarbons also comprise methane not steam-reformed in section (14) of the diagram.

The accompanying drawing is a flow-sheet illustrating the operation of a process according to the invention, by way of example.

A charge (natural gas, e.g. methane or at least one other light hydrocarbon or a mixture of such gases) is fed through lines 1 and 5 to the steam-reforming zone 14. The line for introduction of steam and that for recovering condensate are not shown. Additional carbon dioxide issuing at least partly from the natural gas field, is introduced through lines 2 and 26. Recycle carbon dioxide and hydrocarbons obtained as by-products of the reaction are introduced through line 3. Optionally, line 4 also supplies carbon dioxide recovered at the output of the steam-reforming zone. The steam-reforming zone preferably operates between 730 and 890°C under a pressure from 1 to 4 Megapascals and at a rate of 2000 to 10 000 volumes of gas (normal temperature and pressure) per volume of catalyst and per hour.

The effluent from the steam-reforming zone, withdrawn through line 6, is fed through lines 7 and 8 to a compressor 19. Optionally a portion of the effluent is conveyed, through lines 15 and 16, across a zone 18 wherein a portion of the carbon dioxide from the steam-reforming effluent is recovered by any convenient means, said portion being at least partly fed to the steam-reforming zone 14, through lines 4 and 26. By this way 30 to 60% by mole of the carbon dioxide withdrawn from the steam-reforming reactor are advantageously fed back to said reactor. This recycled carbon dioxide amounts itself to a proportion, by mole, of about 30 to 60% of the total carbon dioxide

introduced into the steam-reforming unit. The effluent from the steam-reforming zone, compressed to the pressure required in the alcohol synthesis zone 20 (generally a pressure from 5 to 20 Megapascals) is supplied through lines 17 and 9 to the catalytic zone 20 for the alcohol synthesis, conveniently operating between 200 and 400°C, preferably between 250 and 350°C.

The effluent from zone 20, withdrawn through line 10, is separated in zone 21 into, on the one hand, a liquid phase containing water and alcohols, said liquid phase being withdrawn through line 12 and, on the other hand, a gaseous phase essentially containing unconverted gases, light hydrocarbons and CO_2 , said gaseous phase, substantially free of water and alcohols, being withdrawn through line 22. At least a portion of said gaseous phase, optionally brought to the temperature prevailing in the steam-reforming zone 14, is recycled to said zone 14 through line 3. Generally 2 to 15% and preferably 2.5 to 10% of the total volume of the gaseous phase of line 22 are thus recycled, so as to obtain preferably a molar ratio "recycled CH_4 /fresh CH_4 " ranging from 0.2 to 2 (preferably from 0.3 to 1), in order to stabilize the reaction equilibrium (2) in direction B.

It is also appropriate to recycle at least a portion of the gaseous phase from line 22 to the alcohol synthesis zone 20, through line 11, compressor 24 and line 25. Advantageously 85 to 98% and preferably 90 to 97.5% by volume of the total gaseous phase are recycled. Finally a portion of the gaseous phase may also be removed (purge) through line 13, said removed portion of the gaseous phase amounting to a maximum of 10% by volume of total gaseous phase of line 22.

The alcohol synthesis is conveniently conducted under a pressure from 5 to 25 Megapascals (MPa), preferably from 6 to 20 MPa; the reaction temperature is conveniently from 200 to 400°C and preferably from 250 to 350°C; the hourly volume velocity (expressed in volumes N.T.P. of gaseous mixture per volume of catalyst and per hour) is usually from 500 to 60 000 h^{-1} and preferably from 2000 to 20 000 h^{-1} .

Many types of catalysts described for said reaction, particularly those of the patents mentioned above in the present specification, are preferably convenient for carrying out the present invention, in particular the catalyst based on copper, cobalt and various other metals, as described in the French Patent No. 2 523 957 and the French Patent application No. 83/05 727 of April 6, 1983, said preferred catalysts providing for the better results when proceeding to the critical recyclings forming the object of the invention. The higher alcohol homologs obtained by the present process are particularly ethanol, propanol, butanol, pentanol, hexanol, heptanol, etc...

EXAMPLE

Methane steam-reforming (zone 14) is conducted at a temperature of 880°C, at an operating pressure of 2 Megapascals, with a water/methane ratio of 2.72 (by volume), at a hourly volume velocity of 5 000 h^{-1} (normal temperature and pressure). The steam-reforming reactor contains 50 metric tons of nickel-alumina-calcium-potassium catalyst (containing by weight: 20% NiO , 5% KOH , 60% alumina and 15% Ca

(OH)₂).

There is no purge (no line 13 provided therefor). A portion of the gaseous phase from line 22 after heating to 880°C, is recycled to the first step and another portion to the second step. CO₂ is recycled through line 4.

The alcohol synthesis reaction section (zone 20) comprises two serially arranged reactors, each of which comprises several catalyst beds, with the provision of intermediary cooling means. The catalyst prepared according to the teaching of French Patent No. 2 523 957 complies with the formula (in atoms) Cu_{0.8} Co_{0.35} Al_{1.1} Zn_{0.5} La_{0.1} Na_{0.2}. Each reactor contains 6 tons of catalyst; the operating pressure is 13 Megapascals and the temperature 300°C.

H₂/CO molar ratio at the input of zone 14 (i.e. in line 5): 1.81.

H₂/CO molar ratio at the input of zone 20 (i.e. in line 9): 1.97.

Gaseous phase recycled through line 3 in percent of the total gaseous phase of line 22 : 3.25%.

CO₂ recycled to line 3 in percent of the total CO₂ of

line 22 : 3.25%.

CO₂ recycled to line 3 in percent of the total CO₂ of line 5 (steam-reforming input) : 14.42%.

% of the gaseous phase recycled to the synthesis zone : 96.74% (by volume).

$$\frac{\% \text{ of CO}_2 \text{ of line 4}}{\% \text{ of CO}_2 \text{ of line 6}} = 0.51 \text{ (molar ratio)}$$

$$\frac{\% \text{ of CO}_2 \text{ of line 4}}{\% \text{ of CO}_2 \text{ of line 5}} = 0.47 \text{ (molar ratio)}$$

$$\frac{\% \text{ of CH}_4}{\% \text{ of fresh CH}_4} = 0.48 \text{ (molar ratio)}$$

The following table gives the balance in kilomoles of the process. The steam partly consumed in section 14 has not been mentioned.

BALANCE IN KILOMOLES

ref. to line of diagram	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
substance												
H ₂			12.5		12.5	135.0	65.2	135.0	503.9	381.6	368.9	0.2
CO			6.9		6.9	51.9	25.05	51.9	255.8	211.1	203.9	0.3
CO ₂		12.23	4.7	15.0	31.93	29.0	14.0	14.0	153.9	146.0	139.9	1.4
CH ₄	29.00		13.80		42.80	5.7	2.75	5.7	412.4	421.3	406.7	0.8
C ₂ (HC)			1.30		1.30	0	0	0	36.55	38.0	36.55	0.15
C ₃ (HC)			0.55		0.55	0	0	0	16.30	17.0	16.30	0.15
C ₄ (HC)			0.18		0.18	0	0	0	6.10	6.40	6.10	0.10
CH ₃ OH									4.10	25.80	4.10	21.70
C ₂ H ₅ OH									0.65	4.20	0.65	3.55
C ₃ H ₇ OH									0.20	1.40	0.20	1.20
C ₄ H ₉ OH									0.10	0.90	0.10	0.80
C ₅ H ₁₁ OH												
C ₆ H ₁₃ OH												
H ₂ O									1.20	34	1.20	32.8
SUM =	29.00	12.23	39.93	15.0	96.16	221.6	107	206.6	1391.2	1287.7	1184.6	63.15

N.B. : line 13 is omitted (no purge)

CLAIMS

1. A process for producing a mixture of methanol with at least one higher alcohol said process comprising the sets of:

a) passing a mixture of a least one fresh hydrocarbon having 1-4 carbon atoms with steam, a carbon dioxide stream and a first recycle gas stream through a steam-reforming zone at 650-950°C, so as to obtain a synthesis gas comprising hydrogen, carbon monoxide and carbon dioxide,

b) separating a carbon dioxide stream from said synthesis gas and passing a mixture of resultant synthesis gas of decreased carbon dioxide content with a second recycle gas stream through an alcohol synthesis zone,

c) separating the product from step (b) into a liquid

phase comprising water and at least the major portion of the alcohols formed in step (b) and a gas phase comprising hydrogen, carbon monoxide, carbon dioxide and hydrocarbons,

d) dividing the gas phase from step (c) into at least a first gas stream and at least a second gas stream, said first gas stream amounting to 2-15% by volume of said gas phase from step (c) and said second gas stream amounting to 85-98% by volume of said gas phase from step (c),

e) feeding said first gas stream of step (d) to step (a), as said first recycle gas stream and controlling the ratio of said first recycle gas stream to said fresh hydrocarbon passed through said steam-reforming zone to have a molar ratio of hydrocarbon in said first recycle gas stream to said fresh hydrocarbon be-

tween 0.2 and 2 and to obtain a molar ratio of hydrogen to carbon monoxide in the synthesis gas obtained in step (a) from about 2 to 3,

5 f) feeding said second gas stream of step (d) to step (b) as said second recycle gas stream and controlling the proportion of said second recycle gas stream to have a molar ratio of hydrogen to carbon monoxide in said mixture passed through said alcohol synthesis zone from 1.6 to 2.4, and

10 g) admixing said carbon dioxide stream of step (b) with said fresh hydrocarbon of step (a) to constitute at least a portion of said carbon dioxide stream of step (a).

2. A process according to claim 1 wherein up to 15 10% by volume of said gas phase separated in step (c) is purged.

3. A process according to either of claims 1 and 2 wherein the volume of first said gas stream recycled to step (a) is from 2.5% to 10% of the total volume of 20 said gas phase from step (c), the molar ratio of hydrocarbon in said first recycled gas stream to said fresh hydrocarbon being from 0.3 to 1 and the volume of said second gas stream recycled to step (b) being from 90 to 97.5% of the total volume of said gas phase 25 from step (c).

4. A process according to any one of the preceding claims wherein said first gas stream recycled to step (a) is pre-heated to 650-900°C.

5. A process according to any one of the preceding 30 claims wherein the alcohol synthesis zone of step (b) is at a temperature from 250 to 350°C, under a total pressure from 6 to 20 Megapascals.

6. A process according to any one of the preceding claims wherein the carbon dioxide stream separated in step (b) represents 30-60% by mole of the 35 total amount of carbon dioxide of the synthesis gas of step (a) and 30-60% by mole of the total amount of carbon dioxide of the mixture passed through the steam-reforming zone of step (a), the molar ratio of 40 hydrogen to carbon monoxide of step (e) is 2.2 - 2.8 and the molar ratio of hydrogen to carbon monoxide of step (f) is 1.8 - 2.2.

7. A process for producing a mixture of methanol with at least one higher alcohol substantially as 45 herein described with reference to the accompanying drawing.

8. A process for producing a mixture of methanol with at least one higher alcohol substantially as herein described in the Example.

50 9. Apparatus for producing a mixture of methanol with at least one higher alcohol substantially as herein described with reference to the accompanying drawing.

10. Each and every novel process, method, compound, composition and apparatus substantially as 55 herein described.